The Tricarbonylchromium Complex of a Trimethyltin-Substituted *N*-(Triisopropylsilyl)indole − A Dynamic NMR Study of Multiple Independent Rotation Processes in the Solid State with an X-ray Diffraction Structure and Molecular Mechanics Calculations

Abil E. Aliev,[a] J. Edgar Anderson,*[a] David Butler,[a] Jorge Gonzalez-Outeiriño,[a] Lodovico Lunazzi,*[b] Andrea Mazzanti,[b] Jonathan W. Steed,[c] and René Wilhelm[d]

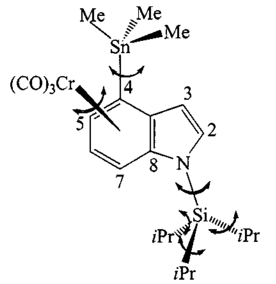
Keywords: NMR spectroscopy / Solid-state structures / Tin / Chromium / Molecular modeling / X-ray diffraction

The title compound was studied by dynamic NMR spectroscopy in solution and in the solid state, and by MM3 molecular mechanics calculations of model compounds. Barriers to rotation of the trimethyltin group, the tricarbonylchromium group, the triisopropylsilyl group, and the isopropyl groups were all too small to measure by NMR in solution i.e. less than about 5 kcal/mol. All of these barriers could be measured, however, in the solid state, are of different sizes, and are surprisingly large, up to 12.9 kcal/mol. A crystal structure determination shows close intermolecular interactions of these triple rotors that explain these high rotation barriers.

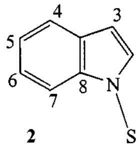
Introduction

Dynamic NMR studies of intramolecular motions in the solid state promise to provide particularly interesting insights when energy barriers found are markedly different from those in solution. Rotational barriers in the solid state are expected to be higher than in solution, since the lattice will usually further hinder any intramolecular process.[1,2] A crystal structure provides direct information on intermolecular interactions that may explain these differences. We now report an investigation of the title compound **1** with a variety of triple rotors.[3] Rotations involve the trimethylstannyl group, the tricarbonylchromium group, and all four bonds to the silicon atom in the *N*-(triisopropylsilyl) (*N*-TIPS) group, so six different bonds in all were investigated. Each rotation has a substantial barrier in the solid state, yet all the corresponding processes in solution were fast on the NMR timescale at all accessible temperatures.

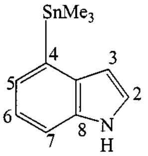
An X-ray diffraction study shows that these groups are strongly hindered by groups in neighbouring molecules, but since barrier sizes are different, the rotations do not appear to be correlated. The parent *N*-(triisopropylsilyl)indole (**2**) was also studied by dynamic NMR in order to assist in elucidating the conformational process in the *N*-TIPS group. Furthermore, MM3 molecular mechanics calculations[4] were carried out on **2** and on 4-(trimethylstannyl)indole (**3**).



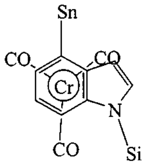
1



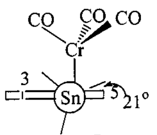
2



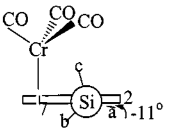
3



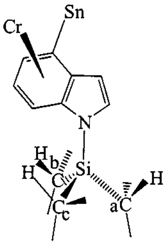
4



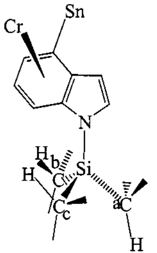
5



6



7, (a, b, c) = (g, -g, g)



8, (a, b, c) = (g, -g, a)

---

[a] Chemistry Department, University College,
Gower Street, London, WC1E 6BT, United Kingdom
E-mail: j.e.anderson@ucl.ac.uk
[b] Dipartimento di Chimica Organica, "A. Mangini", Universita di Bologna,
Viale Risorgimento 4, 40136 Bologna, Italy
E-mail: lunazzi@ms.fci.unibo.it
[c] Chemistry Department, King's College,
Strand, London, WC2R 2LS, United Kingdom
[d] Chemistry Department, Imperial College,
London, SW7 2AZ, United Kingdom

1434−1948/02/0101−0133 $ 17.50+.50/0

Results

Structure

The NMR results are best interpreted in terms of the molecular structure found in the crystal, with some assistance from MM3 calculations for an isolated molecule of the parent *N*-(triisopropylsilyl)indole (**2**), so these structural studies will be reported first. It should be noted that the solution or gas-phase conformations might be different from that of the crystal, particularly for the *N*-TIPS group. The structure of **1** in the crystal is shown in Figure 1 along with two different representations of parts of the unit cell to indicate intermolecular interactions.

The compound is chiral and there are four molecules of each enantiomer in the unit cell. Figure 1 (a and b), show a molecule in the crystal with the (*S*) configuration, based on C(11) as the chiral centre in that diagram, with Sn, Cr, C(6), and C(10) as substituents.[5] Equally, diagrams **1**, and **4**−**7** show the (*S*) configuration, and the discussion below refers to this. As many molecules exist in the (*R*) configuration in the crystal and in solution, with torsion angles of opposite sign,[6] so the discussion could be extended mutatis mutandis to cover them. Greater detail of the crystal structure is given in the Exp. Sect.

The tricarbonylchromium conformation is as in formula **4**. Both the trimethyltin and TIPS groups are in *peri* positions on the indole ring, and have a conformation with two substituents R towards the other *peri* position on either side of the plane and the third substituent close to the plane away from the *peri* interaction, as shown diagrammatically[6] in **5** and **6**. Within the *N*-TIPS group, the isopropyl group conformations can be defined by the $\mathrm{N-Si-C-H^n}$ torsion angles, and in the crystal these are (*g*, −*g*, *g*) for the groups a−c in the order shown in **6**. Thus reasonably, the two out-of-plane isopropyl groups that flank the *peri* position have their methine proton nearest to that position (see **7**). Molecular mechanics calculations for *N*-(triisopropylsilyl)indole (**2**) located a range of minima, each of which, like **6**, has one Si−*i*Pr bond near to the plane close to the C-2 position of the indole ring. These con-

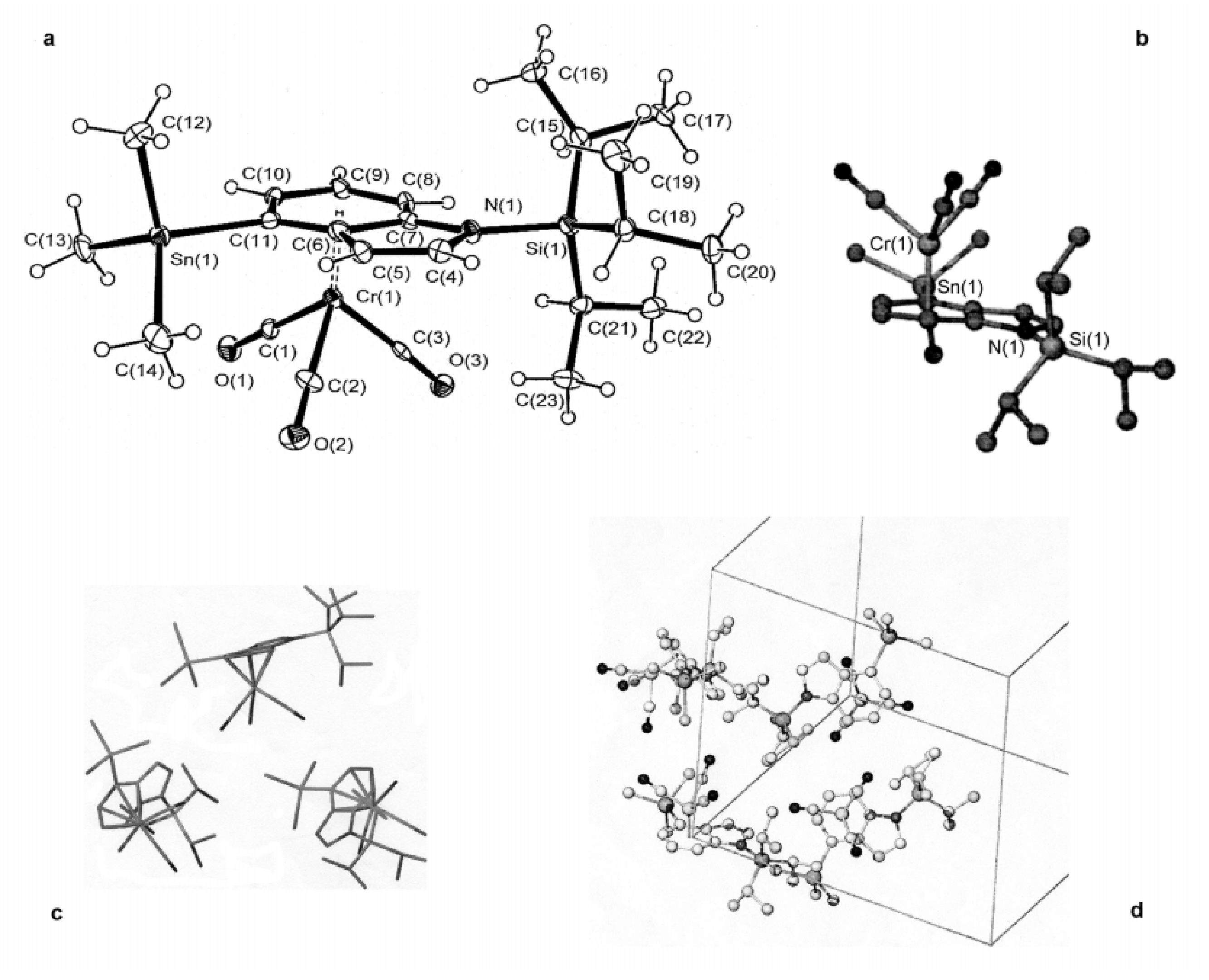
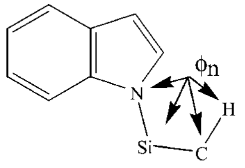
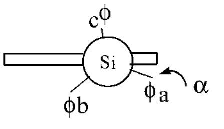


Figure 1. Crystal structure of compound **1**; a, b: ORTEP view and a view (≡ **6**) of the (*S*) configuration, respectively; c, d: parts of the unit cell

formational minima, listed in Table 1 along with the experimentally determined conformation for **1**, differ in the rotational arrangement of the three isopropyl groups as defined by the three N−Si−C−H torsion angles.[7−11] The most stable conformation, as shown in diagram **8**, is (*g*, −*g*, *a*) rather than (*g*, −*g*, *g*) (diagram **7**), which is calculated to be 1.19 kcal/mol less stable, but is the conformation found in the crystal. The structural difference between **7** and **8** is quite small, involving little more than 120° of rotation of the isopropyl group nearest to the tricarbonylchromium group. The calculated and measured torsion angles for the conformation **7**, found in the crystal, agree well.

Table 1. MM3 calculations of steric energies of conformations of *N*-(triisopropylsilyl)indole (**2**); conformations are described by the angle α, the torsion angle φ_a made with the indole plane by the isopropyl group, and the H−C−Si−N torsion angles φ_n, quoted in the alphabetical order shown; the experimental values for the (*g*, −*g*, *g*) conformation are included beneath the calculated values for that conformation





Conformation		Relative steric energy [kcal/mol]	α	φ_a	φ_b	φ_c
(*g*, −*g*, *a*)	**8**	0.00	−14	50	−71	−177
(*a*, *g*, −*g*)		1.14	0	180	79	−78
(*g*, −*g*, *g*)	**7**	1.19	−4	48	−79	48
(*g*, −*g*, *g*)	[a]	–	−11	46	−81	56
(*a*, −*g*, −*g*)		1.44	−14	171	−81	−63
(*a*, −*g*, *a*)		1.66	−12	−173	−55	−151
(*g*, −*g*, −*g*)		2.08	−14	49	−78	−82
(−*g*, −*g*, −*g*)		3.16	−12	−40	−55	−55
(*a*, *a*, *a*)		6.53	−8	−174	135	153

[a] Crystal values for compound **1**.

NMR Spectra

In the ^{13}C NMR spectrum of compound **1** in solution at room temperature, a set of signals corresponding to rapid rotation of all groups is seen, and at 133 K the singlets from the trimethyltin and isopropylsilyl groups are essentially unchanged with no sign of incipient dynamic broadening. While the carbonyl carbon signal is so broad as to be undetectable at this low temperature, this appears to be an effect of relaxation rather than a dynamic process. We conclude that all rotations are still fast on the NMR timescale for compound **1** *in solution* at that low temperature, so the associated barriers would be less than about 5 kcal/mol.

Several regions of ^{13}C CPMAS NMR spectra of crystalline compound **1** under various conditions are shown in Figures 2, 3, and 4, and described fully in the Exp. Sect. While the signals of the isopropyl methyl carbon atoms and aromatic carbon atoms are quite sharp at room temperature (line width at half-height $\Delta\nu_{1/2} \approx 50-60$ Hz), the isopropyl methine ($\Delta\nu_{1/2} \approx 90$ Hz), the trimethyltin ($\Delta\nu_{1/2} \approx 120$ Hz), and carbonyl ($\Delta\nu_{1/2} \approx 250$ Hz) signals are very broad. In contrast to the solution behaviour, all of the signals, except those for aromatic carbon atoms, show dynamic behaviour as the temperature is lowered, eventually showing decoalescence over different temperature ranges, suggesting three different conformational processes. We will discuss these in turn.

As the temperature was lowered from ambient, the broad trimethyltin carbon signal in the CPMAS spectrum sharpened and became more intense initially, then broadened in a conventional dynamic sense, and eventually split below about 233 K to give three singlets, see Figure 4 (spectra at 213 K and 173 K). A complete line-shape treatment yields rate constants at a series of temperatures (see Table 2), and a barrier to rotation in the solid state of 11.1 kcal/mol.

The room-temperature singlet due to the isopropyl methine carbon atoms in the CPMAS spectrum of **1** broadened rather more noticeably than the methyl singlet and split below about 273 K into what eventually became three equal signals. That methyl carbon singlet split below about 253 K into six signals, two of which overlapped. The variable-temperature spectra are shown in Figure 4, and chemical shifts are listed in Table 4 in the Exp. Sect. A complete line-shape fit of spectra at several temperatures led to rate constants shown in Table 2 and a barrier to rotation of about 12.9 kcal/mol for conformational interconversion of the TIPS group in the solid state. As the temperature was raised from room temperature, both signals of the isopropyl carbon atoms broadened compared with others in the spectrum.

The broad signal for the carbonyl carbon atoms in the CPMAS spectrum at room temperature disappeared completely at about 253 K as the temperature was lowered, and reappeared as a very broad singlet at about 213 K. This signal increased in intensity and split at about 193 K to appear at 173 K as a 1:1:1 triplet, see Figure 3. A complete line-shape fit of spectra towards the low-temperature limit could not be achieved, suggesting that the broadening e.g. at 193 K was not due to conformational exchange. Thus, with such an exchange, the peak at $\delta \approx 233$ should have been broader than the two peaks at $\delta \approx 240$ at 193 K, but it was not. The appearance as a singlet above room temperature but as a triplet at 173 K nonetheless indicates that rotation of the tricarbonylchromium group had become slow. This together with a consideration of the temperature range suggests the barrier is between 8 and 12 kcal/mol.

Each of these signals we have discussed showed additional changes at temperatures above the conventional dynamic-NMR range involving broadening and more or less disappearance of singlet signals as the temperature was further raised. In two cases and putatively in the third this was followed by a resharpening of the singlet signals at even higher temperatures. These not unprecedented

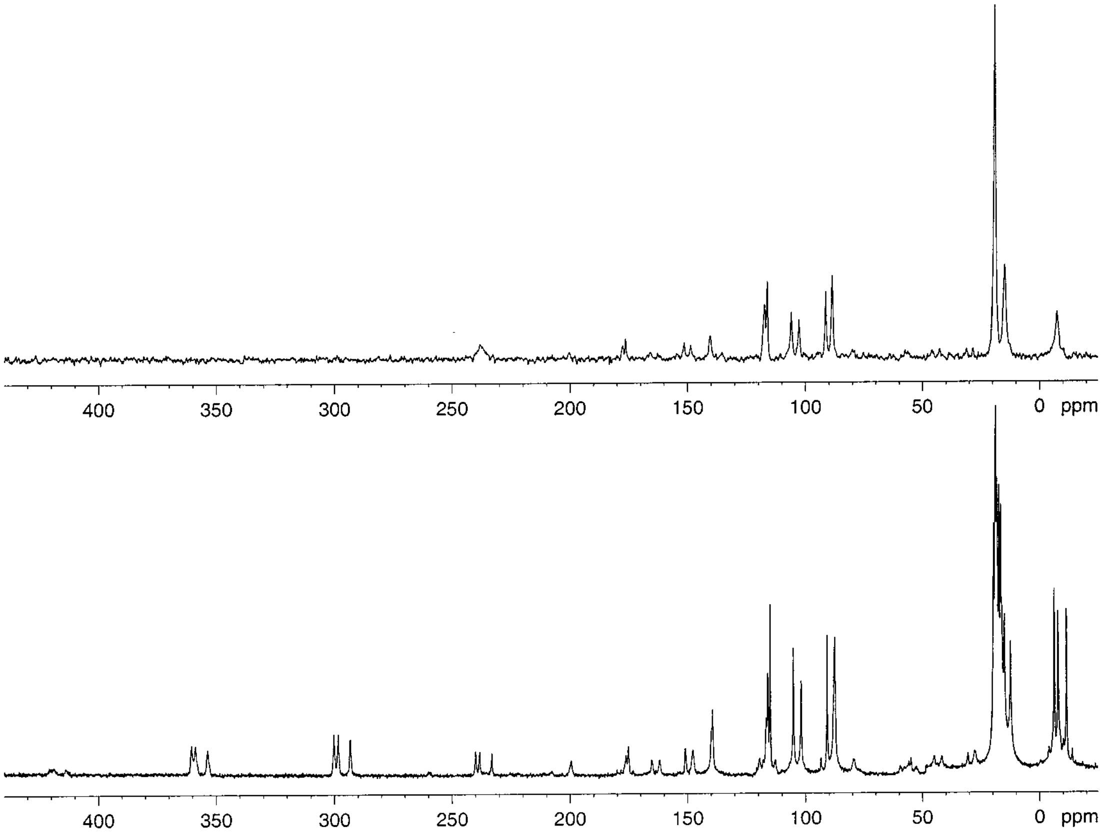


Figure 2. CPMAS ^{13}C NMR spectra of compound **1** at 173 K (bottom) and 297 K (top) − the more intense peaks are between δ = −12 and +22, between δ = +85 and +120, and between δ = +232 and +242; other peaks are side-bands

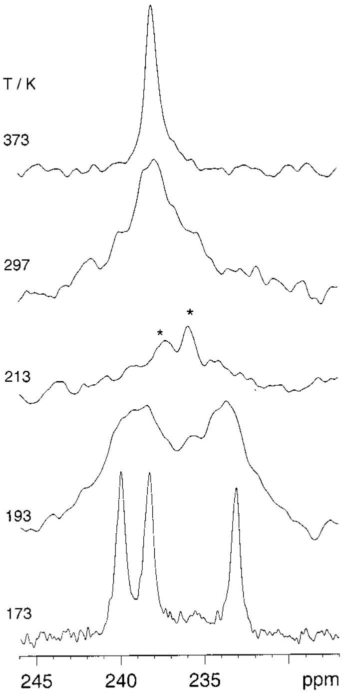


Figure 3. CPMAS ^{13}C NMR spectra of the carbonyl region of compound **1** at various temperatures; * indicates side-bands

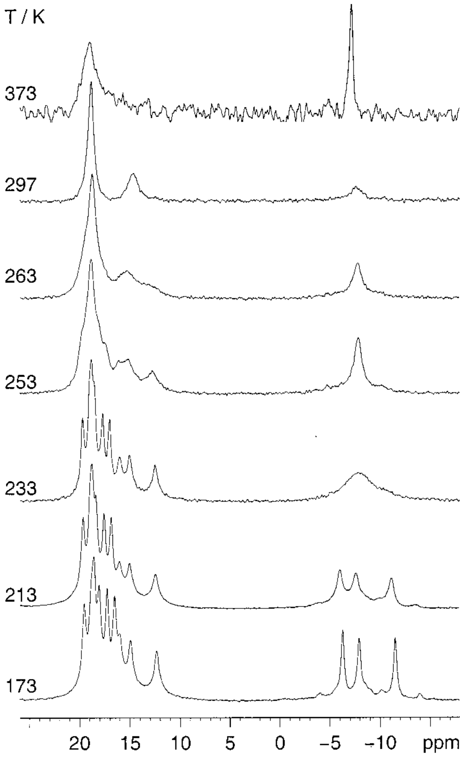


Figure 4. CPMAS ^{13}C NMR spectra of the upfield region of compound **1** at various temperatures

Table 2. Rate constants $[s^{-2}]$ for rotation in compound **1** from complete line-shape analysis in NMR spectra

Temperature	*N*-TIPS rotation	$SnMe_3$ rotation
275 K	400	
268 K	180	
260 K	70	2500
245 K		600
238 K		400
230 K		120

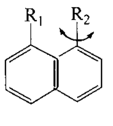
observations[12−14] are a feature of dynamic NMR spectroscopy in the solid state and will be discussed below.

The striking result, therefore, for compound **1** is the NMR observation of three different dynamic processes with barriers up to 12.9 kcal/mol in the solid state. These processes are taking place at a much greater rate in solution, meaning that all barriers must be less than 5 kcal/mol.

Discussion

The barrier of 11.1 kcal/mol for rotation of the trimethyltin group in the solid state is remarkable. Such a symmetrical threefold rotation process of an MR_3 group attached to an aromatic ring should have a low barrier. Thus, the barrier to rotation of a *tert*-butyl group on a benzene-type ring is less (perhaps much less) than 5 kcal/mol, since such barriers have been determined by dynamic NMR in solution only when there was an adjacent *ortho* or *peri* substituent.

Trimethyltin group rotation barriers should certainly be markedly smaller than this, since the four longer Sn−C bonds (211−215 pm) reduce steric hindrance compared with C−C bonds (153−155 pm) in a *tert*-butyl group. There is both experimental and computational evidence confirming that the trimethyltin rotation barriers are very small in the fluid state. Thus, in 1,8-bis(trimethylstannyl)naphthalene (**9**), the barrier is 4.7 kcal/mol,[15] whereas in 1,8-di-*tert*-butylnaphthalene (**10**), the *tert*-butyl group rotational barrier is about 6.5 kcal/mol.[16] The presence of two rotors may of course mean that these are not simple rotation processes.



9 $R_1 = R_2 = SnMe_3$
10 $R_1 = R_2 = CMe_3$
11 $R_1 = H,\ R_2 = CH_2CMe_3$
12 $R_1 = H,\ R_2 = N(iPr)_2$
13 $R_1 = H,\ R_2 = Si(iPr)_3$

Table 3 shows molecular mechanics calculations (MM3) of rotational barriers in an isolated molecule in a series of trimethylstannyl- and *tert*-butyl-substituted aromatic compounds. The calculated values for trimethylstannyl group rotation barriers are very much smaller than those for *tert*-butyl groups, and clearly fall well below the range that might be measured by dynamic NMR studies even under the most favourable circumstances.

Table 3. MM3 calculated rotational barriers [kcal/mol] for *tert*-butyl and trimethyltin aromatic compounds

	Rotational barrier X = C	Rotational barrier X = Sn
Me_3X−benzene	0.46	0.03
1-Me_3X−naphthalene	3.67	1.97
4-Me_3X−indole	2.18	1.05

The fact that barriers are threefold, involving 120° of rotation, is one reason for their small size. Interestingly, higher, NMR-accessible rotational barriers have been found for less symmetrical $MR^1R^2R^3$ substituents when the rotation is twofold or even more so, onefold. Thus for 1-substituted naphthalenes, a barrier of 5.3 kcal/mol has been measured for 1-neopentylnaphthalene (**11**) (twofold)[17] and of 15.3 kcal/mol for 1-(diisopropylamino)naphthalene (**12**) (onefold).[18] These various points combine to suggest that the trimethylstannyl group rotation barriers should be very low for **1** in solution. The 11.1 kcal/mol barrier observed for the trimethylstannyl group rotation in **1** in the solid state is thus surprisingly high and is presumably due almost completely to interactions beyond the molecule itself.

There has already been some exploration,[7−11] of the conformational possibilities for three isopropyl or similar groups attached to a tetrahedral atom, including triisopropylsilyl groups.[10,11] The most recent report[11] includes results both in solution and the solid state for compound **13** with a TIPS group attached to the 1-position in naphthalene. All the more stable conformations calculated have the same arrangement about the C(ring)−Si bond analogous to **6**, with one isopropyl group close to the plane of the ring towards the 2-position. This, unsurprisingly, is the same conformation we now report for the N−Si bond of compound **1** both in the crystal and by calculation.

The conformation about the three Si−diisopropyl bonds has to be considered next, since each C−Si−C−H torsion angle in **13** and each N−Si−C−H torsion angle in **1** can be either +*gauche* or −*gauche* or *anti*, see **7** and **8**. The crystal structure of **1** shows the (*g*, −*g*, *g*) conformation, but information beyond this depends on NMR observations and calculations.

The solution NMR of compound **13** is much more interesting than that of compound **1**, since processes become slow on the NMR time scale at low temperatures and two different more or less equally populated conformations interconvert slowly at about 128 K. At even lower temperatures interconversion of isopropyl groups within these conformations became slow, the barriers to these processes being between 5.7 and 6.25 kcal/mol. In contrast, the solution spectra of compound **1** and of *N*-(triisopropyl)indole (**2**) are temperature-independent, so barriers are significantly lower.

In the solid state, NMR shows that compound **13** persists in adopting two conformations that show distinct spectra below about 223 K. Distinct barriers to rotation about the different C−Si bonds could not be determined from the spectra, but rotation in the lattice has a barrier about 5 kcal/mol greater than in solution.

The ^{13}C NMR results for the TIPS group of compound **1** in the solid state can readily be interpreted in terms of the bond conformations found in the crystal structure. The changes in the isopropyl group signals lead to a barrier of 12.9 kcal/mol, compared with less than 5 kcal/mol in solution, but they cannot be used to distinguish the N−Si and the three C−Si bond rotations.

MM3 calculations suggest (see Table 1), that the (*g*, −*g*, *g*) conformation for **1** has torsion angles gratifyingly similar to those found in the crystal, but that this conformation is about 1.19 kcal/mol less stable than the (*g*, −*g*, *a*) conformation and 0.04 kcal/mol less stable than the (*a*, −*g*, *g*) conformation. This last conformation is too symmetrical to explain the low-temperature NMR spectra, except by invoking an unsymmetrical lattice. The fact that the most stable calculated conformation (*g*, −*g*, *a*) is not the one found in the crystal (*g*, −*g*, *g*), need not reflect shortcomings of the calculations, for it may be evidence of a conformational change induced by crystal lattice forces.

In view of the results in Table 3 for calculated barriers to trimethylstannyl group rotation, it is of interest to know the difference in *N*-TIPS rotation barriers to be expected when the 1-naphthyl group of **13** is replaced by the *N*-indolyl group of **1**. Calculation of TiPSi rotational barriers is complicated, however, as one torsion usually entrains another.[10] We therefore calculated the barrier to a simplified 120° rotation about the *peri* bond for **13** and for *N*-TIPS-indole (**2**) in the conformation with isopropyl groups (*g*, *g*, *g*). This is not a very stable conformation, but the calculation is straightforward since the three *gauche* isopropyl group conformations need not rearrange dramatically during the overall rotation. The barrier to rotation about the *peri* bond in these circumstances is calculated to be 5.6 kcal/mol for **13**, and only 3.2 kcal/mol for the indole **2**. Since the experimental solution barrier in **13** is about 6 kcal/mol this suggests that the barrier for reorientation in the TIPS group of **1** in solution be very much less than 5 kcal/mol. In this light, the 11.9 kcal/mol barrier found for **1** in the solid state is uncommonly high.

There have already been extensive NMR[14,19−22] and other studies[14] of the tricarbonylchromium η^6 complexes of aromatic compounds in the solid state. In crystals of the simple highly symmetrical benzene complex,[19] two distinct processes are taking place: Firstly there is an in-plane rotation of the benzene ligand in 60° jumps, with a barrier of 3.7−4.7 kcal/mol. This was studied using solid-state wideline ^2H wideline NMR techniques.[21] Additionally, there is a dynamic process in which tricarbonylchromium fragments rotate by 120° steps with respect to the crystal lattice (a crystallographic mirror plane bisects the molecule) with a barrier of about 17 kcal/mol.

Even more relevant to our work is what is known from NMR studies of tricarbonylchromium complexes of a set of polymethylbenzenes in the solid state.[14] A range of behaviour has been observed, but there are some general features. At low temperatures the carbonyl carbon signal appears either as a 1:1:1 triplet or a 2:1 doublet indicating that reorientation involving the carbonyl group is slow. On raising the temperature, signals broaden and coalesce, then continue to broaden until they disappear. At temperatures between 20 and 40°C and higher, the broad signal reappears and becomes sharper as the temperature rises.

The carbonyl spectrum of compound **1** in the solid state fits with this pattern, but it is interesting to note that for nine of the ten compounds studied,[14] the changes took place over a higher temperature range than for **1**, implying a higher reorientation barrier. The main difference between **1** and the polymethylbenzenes is that close π-stacking of the aromatic rings is absent in the crystal due to the presence of the bulky trimethylstannyl and TiPSi groups. Lattice effects on rotation in **1** are thus less critical.

Only the pentamethylbenzene complex shows the tricarbonylchromium group rotating with a lower barrier, about 7.5 kcal/mol, but in this case the aromatic ring is not reorienting even at room temperature. The barrier is 17 kcal/mol in benzenetricarbonylchromium,[18] and is even higher in the more symmetrical mesitylene and hexamethylbenzene complexes. Since the barriers reflect intermolecular interactions in different crystal environments, too much time should not be spent on comparisons.

The apparent disappearance of the carbonyl signal over a temperature range above coalescence is most likely associated with the very high chemical shift anisotropy of the CO carbon atoms ($\Delta\sigma \approx 430$ ppm). In the intermediate exchange region (relative to the chemical shift anisotropy), the CO line width $\Delta\nu_{1/2}$ will be of the order of $\Delta\sigma$ (ca. 33 kHz), which means that the spin-spin relaxation time (T_2) will be of the order of 10 µs. This is comparable to the dead-time delay used (15 µs in our experiments), hence complete loss of signal intensity for the CO carbon atoms is observed as a result of T_2 relaxation during the dead-time. For aliphatic carbon atoms, on the other hand, $\Delta\sigma$ is near 0 ppm and corresponding T_2 effects can be safely ignored.

The broadening of the $SnMe_3$ signals in the solid-state NMR spectrum as the temperature is raised from 273 K to room temperature, reaches a maximum breadth at about room temperature (Figure 4). This indicates that the bond rotation frequency at this temperature is comparable to the proton decoupling frequency used, and line broadening results.[12−14] Since the decoupling power used corresponds to a frequency of ca. 50 kHz, we can conclude that the frequency of rotation for the ring−Sn bond is of the same order at 297 K, the temperature of maximum signal broadening, whence the rotational barrier is calculated to be 10.9 kcal/mol at this temperature. This barrier value agrees well with that derived independently from the classical dynamic NMR changes at much lower temperatures shown in Figure 4.

In the same way, the two isopropyl carbon peaks at room temperature begin to broaden as the temperature is raised beyond about 353 K, this being more marked with the methine carbon signal. This is attributed to the onset of the same decoupling frequency effect.

A feature that emerges from the crystal structure of **1** is the interaction of adjacent molecules, and this is of course related to the high rotational barriers reported. The crystal is racemic with eight molecules in the unit cell, four of each enantiomer. Figure 1 (c) shows how three molecules of the same configuration are grouped round a central area with each one of the three molecules turning a different feature towards this centre, either a trimethyltin group, a tricarbonylchromium group, or a triisopropylsilyl group. Figure 1 (d) shows other interactions of adjacent molecules. At the top are two molecules whose contact is through the TIPS groups of each; at the bottom, contact is through a TIPS and a trimethyltin group. These and other views of groups of molecules all indicate that the principal interaction of neighbouring molecules is between TIPS and trimethyltin groups, and it is not surprising that these groups have particularly high rotation barriers in the solid state.

We failed to observe any of these exchange processes for **1** by solution NMR even at 133 K. All six rotation barriers clearly become much lower when derivative **1** passes from the solid to fluid solution state, as reported in a number of other cases.

Experimental Section

The synthesis of complex **1** has been described previously.[3]

High-resolution solid-state ^{13}C NMR spectra were recorded at 75.5 MHz with a Bruker MSL300 spectrometer (7.05 T) using a standard Bruker double-resonance magic angle sample spinning (MAS) probe. The samples were fitted into the cylindrical zirconia rotor (7 mm external diameter) and then spun at MAS frequency in the range 3−7 kHz (with stability better than ca. ±5 Hz). High-resolution solid-state ^{13}C NMR spectra were recorded using cross-polarisation (CP), MAS, and high-power ^{1}H decoupling applied during acquisition. Typical operating conditions for ^{13}C CPMAS experiments were: ^{1}H 90° pulse duration = 5 μs; contact time = 1 ms; recycle delay = 2 s. The stability and accuracy of the temperature controller used (Bruker B-VT1000) were ca. ±1 K. The ^{13}C chemical shifts are given relative to tetramethylsilane (Table 4). Fitting of the dynamic NMR changes in the trimethyltin and isopropylmethine signals with temperature was on the basis of a three-site mutual exchange. Fitting of the isopropylmethyl signal was on the basis of a six-site mutual exchange, which may not be strictly appropriate, but in view of the small chemical shift range of the six signals is likely to yield a reasonable approximation for that signal. Details of the crystal structure determination are shown in Table 5. Crystals were mounted on a thin glass fibre using silicon grease and cooled on the diffractometer to 100 K using an Oxford Cryostream low-temperature attachment. Approximate unit cell dimensions were determined by the Nonius Collect program[23] from 5 index frames of width 2° in using a Nonius Kappa CCD diffractometer, with a detector-to-crystal distance of 30 mm. The Collect program was then used to calculate a data collection strategy to 99.5% completeness for 2θ = 27.5° using a combination of 2° and ω scans of 10 s·deg^{-1} exposure time. Crystals were indexed using the DENZO-SMN package[24] and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO-SMN, Scalepack[24]) resulted in unique data sets corrected for Lorentz and polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Structures were solved using SHELXS-97[25] and developed by alternating least-squares cycles

Table 4. NMR spectroscopic data for compound **1**

	^{13}C, solution Ambient temp.	^{13}C, solid state Ambient temp.	^{13}C, solid state 183 K	^{1}H, solution Ambient temp.
C=O	236.2	238	233.1 238.2 239.9	
aromatic	84.0, 89.1 97.9, 106.8 138.5	88.5, 91.3 102.7, 105.9 116.2, 117.5 140.3	87.5, 90.7 101.8, 105.0 115.0, 116.0 139.3	5.10 (1 H) 6.35 (1 H) 7.1−7.5
*i*Pr CH_3	18.1	18.9	19.5, 18.6, 18.1 17.3, 16.5	1.20
*i*Pr CH	12.8	14.7	12.4, 15.0, 16.5	1.70
Sn CH_3	−8.2	−7.5	−6.3, −7.9, −11.5	0.5

Table 5. Crystal data and structure refinement for $[Cr(CO)_3SnMe_3C_8H_5NSi(iPr)_3]$

Identification code	sntipsa
Empirical formula	$C_{23}H_{35}CrNO_3SiSn$
Molecular mass	572.30
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	*Pbcn*
Unit cell dimensions	a = 17.1962(19) Å
	b = 18.1537(19) Å
	c = 16.717(2) Å
Volume	5218.6(10) Å
Z	8
Density (calculated)	1.457 Mg/m^3
Absorption coefficient	1.442 mm^{-1}
$F(000)$	2336
Crystal size	0.20 × 0.20 × 0.15 mm
θ range for data collection	2.04 to 27.50°.
Index ranges	$-22 \le h \le 19$
	$-23 \le k \le 22$
	$-21 \le l \le 19$
Reflections collected	21815
Independent reflections	5909 [R(int) = 0.1597]
Completeness to θ = 27.50°	98.6%
Max./min. transmission	0.8128/0.7614
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	5909/0/281
Goodness-of-fit on F^2	0.942
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0549, $wR2$ = 0.0974
R indices (all data)	$R1$ = 0.1414, $wR2$ = 0.1222
Extinction coefficient	0.00014(8)
Largest diff. peak and hole	1.109 and −0.910 e·Å^{-3}

and difference Fourier synthesis (SHELXL-97[3]) with the aid of the program XSeed.[26] All non-hydrogen atoms were modelled anisotropically, while hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride. All calculations were carried out with either a Silicon Graphics Indy workstation or an IBM-compatible PC. Crystal data for **1**: $C_{23}H_{35}CrNO_3SiSn$, M = 572.30 g·mol^{-1}, orthorhombic, space group *Pbcn*, a = 17.1962(19), b = 18.1537(19), c = 16.717(2) Å, V = 5218.6(10) Å^3, D_c = 1.457 Mg·m^{-3}, Z = 8, μ= 14.42 cm^{-1}, T = 100(2) K, Reflections measured: 21 815, unique data: 5909, parameters: 281, $R1$ [$F^2 > 2\sigma(F^2)$] 0.0549, $wR2$ (all data) 0.1222. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167381. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank the EPSRC and King's College London for the provision of the X-ray diffractometer and the Nuffield Foundation for the provision of computing equipment.

---

[1] [1a] F. G. Riddell, S. Arumugam, K. D. M. Harris, *J. Am. Chem. Soc.* **1993**, *115*, 1881; – [1b] F. G. Riddell, G. Bernath, F. Fulop, *J. Am. Chem. Soc.* **1995**, *117*, 2327.

[2] D. Braga, *Chem. Rev.* **1992**, *92*, 633.

[3] P. J. Beswick, C. S. Greenwood, T. J. Mowlem, G. Nechvatal, D. A. Widdowson, *Tetrahedron* **1988**, *44*, 7325.

[4] N. L. Allinger, Y. H. Yu, J.-H. Lii, *J. Am. Chem. Soc.* **1989**, *111*, 8551.

[5] R. S. Cahn, C. K. Ingold, V. Prelog, *Angew. Chem.* **1966**, *78*, 413; *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 385.

[6] The torsion angles in **5**, **6** are taken from the crystal, but numbering is in terms of diagram **1**. The torsion angle C2–N–Si–C_a is negative in the chiral crystal, so for achiral **2**, calculated conformations for the *N*-TIPS groups will be normalised to the conformation in which this torsion angle is likewise negative.

[7] J. E. Anderson, K. H. Koon, J. E. Parkin, *Tetrahedron* **1985**, *41*, 561.

[8] J. E. Anderson, B. R. Bettels, *Tetrahedron* **1990**, *46*, 5353.

[9] I. Columbus, S. E. Biali, *J. Org. Chem.* **1993**, *58*, 7020.

[10] J. E. Anderson, D. Casarini, L. Lunazzi, A. Mazzanti, *Eur. J. Org. Chem.* **2000**, *65*, 479.

[11] J. E. Anderson, D. Casarini, L. Lunazzi, A. Mazzanti, *J. Org. Chem.* **2000**, *65*, 1729. The conformations for the TIPS group adopted by compound **13** are firstly (*g*, −*g*, *a*) and secondly a rapid equilibration between (*g*, −*g*, *g*) and (*a*, −*g*, *g*).

[12] W. P. Rothwell, J. S. Waugh, *J. Chem. Phys.* **1981**, *74*, 2721.

[13] P. J. Barrie, J. E. Anderson, *J. Chem. Soc., Perkin Trans. 2* **1992**, 2031, and earlier results cited therein.

[14] P. J. Barrie, C. A. Mitsopoulou, M. Motevalli, E. W. Randall, *J. Chem. Soc., Dalton Trans.* **1997**, 353.

[15] F. A. L. Anet, D. Donovan, U. Sjostrand, F. Cozzi, K. Mislow, *J. Am. Chem. Soc.* **1980**, *102*, 5941

[16] J. E. Anderson, R. W. Franck, W. L. Mandella, *J. Am. Chem. Soc.* **1972**, *94*, 4608.

[17] J. E. Anderson, D. J. D. Barkel, *J. Chem. Soc., Perkin Trans. 2* **1984**, 1053.

[18] [18a] D. Casarini, E. Foresti, L. Lunazzi, D. Macciantelli, *J. Am. Chem. Soc.* **1988**, *110*, 4527. – [18b] D. Casarini, S. Davalli, L. Lunazzi, D. Macciantelli, *J. Org. Chem.* **1989**, *54*, 4616.

[19] A. E. Aliev, K. D. M. Harris, F. Guillaume, P. J. Barrie, *J. Chem. Soc., Dalton Trans.* **1994**, 3193, and earlier work cited therein.

[20] P. Delise, G. Allegra, E. R. Mognaschi, A. Chierico, *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 207.

[21] A. E. Aliev, K. D. M. Harris, F. Guillaume, *J. Phys. Chem.* **1995**, *99*, 1156.

[22] P. J. Barrie, C. A. Mitsopoulou, E. W. Randall, *J. Chem. Soc., Dalton Trans.* **1995**, 2125.

[23] R. Hooft, *Collect*, Nonius B. V., Delft, **1998**.

[24] Z. Otwinowski, W. Minor, in *Methods in Enzymology* (Eds.: C. W. Carter, R. M. Sweet), Academic Press, New York, **1996**, vol. 276, pp. 307–326.

[25] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**.

[26] L. J. Barbour, *XSeed, A Program of the Manipulation and Display of Crystallographic Models*, University of Missouri, Columbia, **1999**.

Received June 5, 2001
[I01204]